PATENT SPECIFICATION (11) 1314711

1314711

NO DRAWINGS

(21) Application No. 35894/70 (22) Filed 24 July 1970

(31) Convention Application No. 844 662 (32) Filed 24 July 1969

(31) Convention Application No. 881 284 (32) Filed 1 Dec. 1969 in

(33) United States of America (US)

(44) Complete Specification published 26 April 1973

(51) International Classification C09D 7/00

(52) Index at acceptance
C4A 4M
C5D 1B11A 1B11B 1B11C 1B11D

(72) Inventor THOMAS ALFRED VIVIAN

(54) COMPOSITION FOR REFLOWING ORGANIC SURFACES

(71) We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention relates to a composition for reflowing thermoplastic organic surfaces.

Although various solvents have been used to reflow thermoplastic organic surfaces, heat treatment has been the primary technique used to reflow such surfaces. Of the solvents, chlorinated hydrocarbons are especially effective reflow agents. The greatest drawback to the commercial use of chlorinated solvents on pigmented organic materials, however, has been the marked dicoloration encountered when these solvents are employed. This discoloration is especially troublesome when methylene chloride is used to reflow metallized paints. Also, in reflowing thermoplastic surfaces, crazing and bloom-back are encountered in addition to discoloration.

The above defects and deficiencies have been overcome by the present invention which is a reflow composition containing 50 to 99 per cent by volume of a liquid chlorinated aliphatic hydrocarbon with the remaining 1 to 50 per cent being one or more additional components having a boiling point of below 200°C., and preferably 50—200°C. wherein each of said components is an alcohol, ketone, benzenoid hydrocarbon, glycol ether alkanoate or alkyl alkanoate, or mixture of an alkylene glycol alkyl mono or diether and a benzenoid hydrocarbon.

Preferable reflow compositions are those containing by volume 50 to 90% of a liquid chlorinated aliphatic hydrocarbon, 5 to 30% of a ketone or alcohol, 2 to 20% of a glycol ether alkanoate and 0 to 30% of an alkyl alkanoate, all of such components having a boiling point below 200°C., such compositions have been found to be especially effective reflow agents for thermoplastic organic surfaces such as paint.

Organic surfaces are easily reflowed by the compositions of the present invention by applying the composition to the surface in the form of a liquid by means of a fine spray, or preferably by vaporizing the composition and contacting the surface with a vapor at an elevated temperature. During reflow, the organic surface becomes fluid and is mobilized to form an essentially uniform coat over the supporting body. After reflow, the organic surface dries as the solvent is evaporated under its own vapor pressure at ambient conditions or by heating the reflowed surface. The dried surface forms an essentially identical surface to that of the surrounding area. Thus, by localised reflow, minor imperfections in a small area of an organic surface may be removed without creating noticeable distortions in the color or other characteristics of the total surface. Alternatively, the whole surface may be reflowed to improve gloss in lieu of buffing.

The chlorinated aliphatic hydrocarbon of the composition of the invention may suitably be any normally liquid chlorinated hydrocarbon that is a partial solvent for the organic surface. These chlorinated hydrocarbons preferably have 1 to 6 carbon atoms and a boiling point of less than 200°C. at atmospheric pressure. Although the hydrocarbon backbone may vary widely, best results have been obtained with 2 to 6 chlorine atoms per molecule. According to these general limitations, representative compounds of the present invention include. the chlorinated alkanes such as methylene chloride, chloroform, 1,1- and 1,2 - dichloro - ethane, 1,1,1- and 1,1,2-trichloroethane, the various trichloropropanes,

[*Price 25p*]

tetrachloropropanes, tetrachlorobutanes, hexachlorobutanes, dichloropentanes and trichlorohexanes; and the chlorinated alkenes such as 1,2- *cis*- and *trans*-dichloroethylene, trichloroethylene, tetrachloroethylene, the trichloropropenes and tetrachlorobutenes. In the preferred composition of the present invention, the chlorinated aliphatic component is a chlorinated alkane or alkene of 1 to 3 carbon atoms with methylene chloride, 1,2- *cis*- or *trans*-dichloroethylene, trichloroethylene and tetrachloroethylene being of special interest. Of greatest importance in the present invention is methylene chloride.

Although the chlorinated aliphatic hydrocarbon may comprise 50—99%, and preferably 50 to 90% by volume of the composition of the present invention, compositions containing 60 to 80% of the chlorinated hydrocarbon are preferred. The chlorinated hydrocarbon may also be stabilized against metal reduction with minor amounts of various stabilizers such as propylene oxide, butylene oxide, dimethoxymethane or other suitable stabilizers. The use of such stabilizers is preferred when methylene chloride is the chlorinated aliphatic hydrocarbon.

The remaining 1 to 50% of the reflowing composition in the broadest concept of the present invention may be any alkanol, alkyl alkanoate, glycol ether alkanoate, ketone, benzenoid hydrocarbon, mixture of an alkylene glycol alkyl ether and benzenoid hydrocarbon, or mixture thereof having a boiling point of 50° to 200°C. at atmospheric pressure. Representative examples of such components include: alkanols such as methanol, n-butanol, 2-butanol, isobutyl alcohol, amyl alcohol and hexanol; alkyl alkanoates such as methyl acetate, ethyl butyrate, propyl acetate, n-butyl propionate; alkanones such as acetone, methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, ethyl amyl ketone; benzenoid hydrocarbons such as benzene, toluene, ethyl benzene, o-, m- and p-xylene; and mixtures of alkylene glycol alkyl mono and diethers and benzenoid hydrocarbons such as propylene glycol monomethyl ether and xylene, ethylene glycol monoethyl ether and toluene, butylene glycol diethyl ether and benzene, and propylene glycol monoethyl ether and toluene. Of these various components, butanol, butyl acetate, methyl isobutyl ketone, or propylene glycol monomethyl ether and xylene are preferred.

In the preferred compositions of the present invention, the second component of the reflow composition is a ketone of alcohol which may comprise 5 to 30% by weight of the reflow composition. Such ketones and alcohols are normally liquid at room temperature and have a boiling point of 50° to 200°C. at atmospheric pressure. Representative examples of such ketones and alcohols include: ketones having up to 11 carbon atoms, such as acetone, methyl ethyl ketone, diethyl ketone, methyl propyl ketone, methyl isobutyl ketone, ethyl amyl ketone, di-n-butyl ketone, allyl ethyl ketone, acetyl acetone and methyl hexyl ketone; and alcohols containing up to 8 carbon atoms such as methanol, ethanol, propanol, isopropanol, n-butanol, 2-butanol, pentanol, hexanol, octanol and allyl alcohol. Of these ketones and alchohols, acetone, methyl ethyl ketone, methyl isobutyl ketone and butanol are preferred. Although the concentration of the ketone and alcohol may range from 5 to 30 volume percent, concentrations of 10 to 25 volume percent are preferred.

The third component in the preferred composition of the present invention is a glycol ether alkanoate. Such glycol ether esters have one of the terminal hydroxyls capped with an alkyl ether group and the other hydroxyl capped with an acyl group and may be prepared by reacting a glycol according to ordinary etherification and esterification reactions. Preferred glycol ether esters boil at 140° to 200°C. Representative examples of suitable glycol ether esters include: ethylene glycol ether esters, such as ethylene glycol ethyl ether acetate, ethylene glycol butyl ether acetate, ethylene glycol methyl ether acetate, ethylene glycol methyl ether proprionate, ethylene glycol propyl ether acetate, and ethylene glycol methyl ether butyrate; propylene glycol ether esters, such as propylene glycol ethyl ether acetate, propylene glycol methyl ether acetate, propylene glycol propyl ether acetate, propylene glycol methyl ether propionate, propylene glycol methyl ether butyrate and propylene glycol butyl ether acetate; and butylene glycol ether esters such as butylene glycol ethyl ether acetate, butylene glycol methyl ether acetate, butylene glycol ethyl ether butyratet and butylene glycol butyl ether acetate. Preferred lower alkylene glycol ether esters have an alkyl ether group of 1 to 4 carbon atoms and an acyl group of 2 to 5 carbon atoms. Also preferred in the present invention are the glycol ether esters of ethylene glycol. Especially preferred in the present invention is the use of ethylene glycol ethyl ether acetate. Although the glycol ether acetate may be present in amounts of 2 to 20% by volume, compositions containing 5 to 15% by volume of the glycol ether ester are preferred.

The fourth and optional component of the preferred composition of the present invention is an alkyl alkanoate. Suitable alkyl alkanoates for use in the present invention have a boiling point of 50° to 200°C. and contain 3 to 10 or more carbon atoms. Representative examples of such alkyl alkanoates include methyl acetate, ethyl acetate, butyl acetate, hexyl acetate, ethyl propionate, ethyl butanoate, propyl hexanoate and butyl propionate. The use of butyl acetate is preferred especially when organic surfaces having a temperature of about 30°C. are reflowed. As the temperature of the organic surface is increased, the alkyl alkanoate

of the composition is preferably replaced by the glycol ether ester which is more effective for high temperature applications.

The compositions of the present invention are simply prepared by mixing the individual components in the proportions described above. The reflowing compositions of the present invention may suitably be applied to any organic surface that is at least partially soluble in the reflow composition to remove minor imperfections from localized areas or from the entire surface. The particular reflow composition may vary widely as different organic surfaces and terminal characteristics are desired. Of the various organic surfaces that may be reflowed by the compositions of the present invention, paints including lacquers and enamels, thermoplastic resins, such as polystyrene, polybutadiene, acrylonitrile-butadiene-styrene and similar substances, are preferred, with the reflow of paint being of particular interest.

With the compositions of the present invention, minor imperfections are conveniently and effectively removed from a thermoplastic organic surface by applying a reflow composition of the invention to the surface under conditions which allow for rapid vaporization of the reflow solvent. Generally, the reflow compositions of the invention are volatile enough to be removed under normal room conditions, but some may require heating or other technique to increase the rate of evaporation.

The following examples illustrate the invention.

Examples 1—6

Two large steel sheets were completely painted with aluminized acrylic lacquer and dried. With a coarse piece of sand paper, a 3" wide (7.62 cm.) scratched area was made in the paint along two opposite sides. The steel sheet was then divided into separate areas by masking tape. Various compositions of the present invention were then vaporized and the hot vapors were connected with individual test sections. The test sections were allowed to dry and their appearance was examined. Two tests were run on each of the reflowing compositions—one used a light dose of the reflow composition and the other used a heavy dose. The compositions and results of the experiments are shown in Table 1.

TABLE I

Reflowing Aluminized Acrylic Lacquer

Composition	Light Dose	Heavy Dose
Example 1		
60% Methylene Chloride 25% Propylene glycol monomethyl ether 15% Toluene	Minute scratches remained. No discoloration.	All scratches removed. Slight discoloration.
Example 2		
60% Methylene chloride 25% Propylene glycol monomethyl ether 15% o-Xylene	Minute scratches remained. No discoloration.	All scratches removed. No discoloration.
Example 3		
70% Methylene chloride 30% n-Butanol	Minute scratches remained. Very slight discoloration.	All scratches removed. No discoloration.
Example 4		
70% Methylene chloride 30% o-Xylene	Minute scratches remained. No discoloration.	Minute scratches remained. No discoloration.
Example 5		
60% Methylene chloride 40% Methyl isobutyl ketone.	Minute scratches remained. No discoloration.	Very minute scratches remained. No discoloration.
Example 6		
75% Methylene chloride 25% Butyl acetate	Minute scatches remained. No discoloration.	Very minute scratches remained. No discoloration.

Examples 7—10

Four pieces of steel measuring 12″×6″ (30.5×15.2 cm.) were completely painted on one side with aluminized acrylic lacquer and dried. With a coarse piece of sandpaper, a 3″ wide (7.62 cm.) scratched area was made in the paint along one side. Masking tape was then applied to partially cover the scratched and unscratched painted area. Various compositions of the invention were then vaporized and hot vapors were contacted with the individual test sections to reflow the exposed paint. The test sections were allowed to dry, the mask was removed and the appearance of the reflowed areas was examined in comparison to the part of the metal sheet covered by the masking tape during the solvent reflow operation. The discoloration, characteristics of the reflowed surface and subsequent blistering under high humidity conditions were tested. The blistering experiments were conducted by placing the reflowed metal plate in a chamber at 100% relative humidity and 95°—140°F. (35.0—60.0°C.) for a period of four days shortly after the painted surface had been reflowed and then observing the surface for blistering. The examples were run at 70°F. (21.1°C.) and also at 140°F. (60.0°C.). In each example, the paint was reflowed, minor scratches in the surface were removed, a glossy surface resulted and no blistering was encountered. The compositions and results of the discoloration observations are shown in Table II.

TABLE II

Reflow of Aluminized Acrylic Laquer

Composition, Wt. %	Discoloration	
	70°F. (21.1°C.)	140°F. (60.0°C.)
Example 7		
70% Methylene chloride[1]. 20% Methyl ethyl ketone 10% Ethylene glycol ethyl ether acetate	Faint dull haze Very little discoloration	No haze No discoloration
Example 8		
70% Methylene chloride[1] 20% Acetone 10% Ethylene glycol ethyl ether acetate	Very faint haze Very little discoloration	No haze Very faint discoloration
Example 9		
70% Methylene chloride[1] 20% Methyl ethyl ketone 5% Ethylene glycol ethyl ether acetate 5% Butyl acetate	Faint haze Very little discoloration	Very faint haze Very little discoloration
Example 10		
30% Methylene chloride[1] 20% Acetone 5% Ethylene glycol ethyl ether acetate 5% Butyl acetate	Faint haze Little discoloration	Faint haze Little discoloration

[1]Containing 0.5% by weight propylene oxide.

WHAT WE CLAIM IS:—

1. A composition for reflowing organic surfaces comprising 50 to 99% by volume of a liquid chlorinated aliphatic hydrocarbon and 1 to 50% by volume of one or more additional components having a boiling point of below 200°C., wherein each of said components is an alcohol, ketone, benzenoid hydrocarbon, a glycol ether alkanoate or alkyl alkanoate, or a mixture of an alkylene glycol alkyl mono or diether and a benzenoid hydrocarbon.

2. A composition for reflowing organic surfaces comprising 50 to 99% by volume of a normally liquid chlorinated aliphatic hydrocarbon and 1 to 50% by volume of one or more additional components having a boiling point of 50° to 200°C. wherein each of said components is an alcohol, alkyl alkanoate, ketone, benzenoid hydrocarbon, or a mixture of an alkylene glycol alkyl mono or diether and a benzenoid hydrocarbon.

3. A composition for reflowing organic surfaces as claimed in claim 2 wherein the chlorinated hydrocarbon has 1 to 6 carbon atoms, 2 to 6 chlorine atoms and a boiling point of less than 200°C. at atmospheric pressure.

4. A composition for reflowing organic surfaces as claimed in claim 2 wherein the chlorinated hydrocarbon is a chlorinated alkane or alkene having 1 to 3 carbon atoms.

5. A composition for reflowing organic surfaces as claimed in claim 2 wherein the chlorinated hydrocarbon is methylene chloride, 1,2-cis and trans dichloroethylene, trichloroethylene or tetrachloroethylene.

6. A composition for reflowing organic surfaces as claimed in any one of claims 2 to 5 wherein the chlorinated hydrocarbon component is present in 60 to 80% by volume.

7. A composition for reflowing organic surfaces as claimed in any one of claims 2 to 6 wherein the second component is butanol, butyl acetate, methyl isobutyl ketone or a mixture of propylene glycol monomethyl ether and xylene.

8. A composition for reflowing organic surfaces as claimed in any one of claims 2 to 6 wherein the second component is a mixture of an alkylene glycol alkyl ether and a benzenoid hydrocarbon.

9. A process for reflowing an organic surface comprising applying the composition as claimed in any one of claims 2 to 8 to the surface under conditions which allow for rapid vaporisation of the reflow composition.

10. A process for reflowing an organic surface as claimed in claim 9 wherein the surface is paint or a thermoplastic polymer.

11. A process for reflowing an organic surface as claimed in claim 10 wherein the composition is applied to the surface as a hot vapor.

12. A process for reflowing an organic surface substantially as hereinbefore defined in Examples 1 to 6.

13. A composition for reflowing organic surfaces, consisting of, by volume.

50—90% of a liquid chlorinated aliphatic hydrocarbon,

5—30% of a ketone or alcohol,

2—20% of a glycol ether alkanoate,

0—30% of an alkyl alkanoate,

all of such components having a boiling point below 200°C.

14. A composition as claimed in claim 13 wherein the chlorinated aliphatic hydrocarbon is a chlorinated alkane or alkene of 1—3 carbon atoms.

15. A composition as claimed in claim 13 wherein the chlorinated hydrocarbon is methylene chloride, 1,2-*cis*- and *trans*-dichloroethylene, trichloroethylene or tetrachloroethylene.

16. A composition as claimed in any one of claims 13 to 15 wherein 60 to 80% by volume of the composition is the chlorinated aliphatic hydrocarbon.

17. A composition as claimed in any one of claims 13 to 16 wherein the ketone or alcohol is acetone, methyl ethyl ketone, methyl isobutyl ketone or butanol.

18. A composition as claimed in any one of claims 13 to 17 wherein 10 to 25% by volume is the ketone or alcohol.

19. A composition as claimed in any one of claims 13 to 18 wherein the lower alkylene glycol ether alkanoate has an alkyl ether moiety of 1 to 4 carbon atoms an an acyl moiety of 2 to 5 carbon atoms.

20. A composition as claimed in any one of claims 13 to 19 wherein the lower alkylene glycol ether alkanoate is an ethylene glycol ether alkanoate.

21. A composition as claimed in any one of claims 13 to 20 wherein 5 to 15% by volume is the lower alkylene glycol ether alkanoate.

22. A composition as claimed in any one of claims 13 to 21 containing ethylene glycol ethyl ether acetate.

23. A process for reflowing a thermoplastic organic surface comprising contacting a composition as claimed in any one of claims 13 to 22 with the surface under conditions which allow for rapid vaporisation of the composition.

24. A process as claimed in claim 23 wherein the thermoplastic organic surface is paint.

25. A process as claimed in claim 23 or claim 24 wherein the composition is applied to the surface as a hot vapor.

26. A process for reflowing an organic surface substantially as hereinbefore described in Examples 7 to 10.

BOULT, WADE & TENNANT,
111 & 112 Hatton Garden,
London, E.C.1,
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1973.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.